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Spectroscopic studies of the vibrational and electronic properties of hydrogen at high pressure-temperature conditions

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The behavior of hydrogen at high densities has been widely explored in recent years both experimentally and theoretically, yielding a wealth of information on the material (*e.g.*, Ref. 1). Detailed information has been obtained from static compression experiments generally limited to low-temperature studies (<300 K) and maximum pressures of ≈300 GPa (*e.g.*, Refs. [2,3]). However, there are now numerous questions regarding the behavior of hydrogen at high pressures and temperatures, results that have important implications for both fundamental physics and planetary science.

We report here [2] Raman scattering and visible to near-infrared absorption spectra of solid hydrogen under static pressure up to 285 GPa at 85-140 K. We obtain pressure dependences of vibron and phonon modes in agreement with previously determined to lower pressures. The results indicate the stability of the ordered molecular phase III to the highest pressure reached and provide constraints on the insulator-to-metal transition pressure. Extrapolations of the vibron and phonon frequencies suggest transformation to a monoatomic state below 495 GPa. On the other hand, considerations of the absorption edge indicate the pressure of metallization at 325-385 GPa on the basis of tentative extrapolation of the direct band gap energy. Although complicated by affects of stressed-induced diamond absorption and possible differences between the behavior of the direct and indirect gap, there appears to be an emerging consistence between various experimental and theoretical results, with a predicted transition at 325-495 GPa.

We also report high *P-T* Raman measurements of solid and fluid hydrogen to above 1100 K and to 155 GPa [4]. These conditions, which were previously inaccessible by static compression experiments, provide new insight into the behavior of the material under extreme conditions. The data give a direct measure of the melting curve (Fig. 1) that extends previous optical investigations by up to a factor of four in pressure. The measurements indicate that the melting curve may flatten out [5]. This result is close to the melting line maximum and liquid-liquid transition predicted theoretically [7,8].

The magnitude of the vibron temperature derivative $(d\nu/dT)_P$ increases by a factor of ≈30 (Fig. 2) over the measured pressure range, indicating an increase in intrinsic anharmonicity and weakening of the molecular bond. Moreover, there is an unexpected increase in intensity of the Raman vibron that arises from the combined *P-T* effects on the electronic properties. Overall, the results reveal significant changes in the state of hydrogen at moderate temperatures (≈1000 K) and megabar pressures.

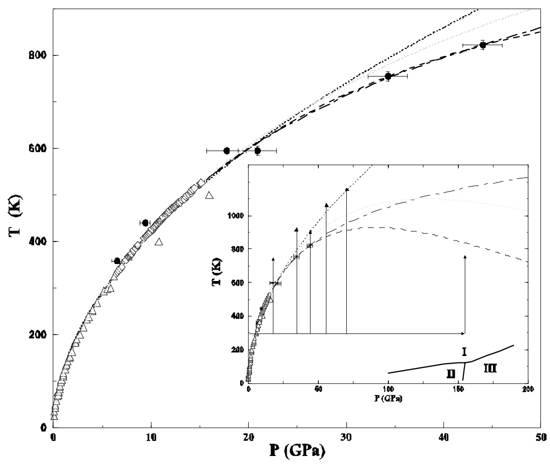

Fig. 1. The melting curve of H_2. The filled circles are from the present work, open diamonds from [5] and open triangles are from [6] and references therein. Different melting laws were fitted to 3 combined data sets: dashed line - Kechin equation; dot-dashed - Kraut-Kennedy equation; dotted - Simon-Glatzel equation. The light gray line shows the Kechin model fit from Ref. datchi. Inset: phase diagram of H_2 with low temperature phases (shown in solid lines). Arrows show various *P-T* paths taken in the higher pressure range.

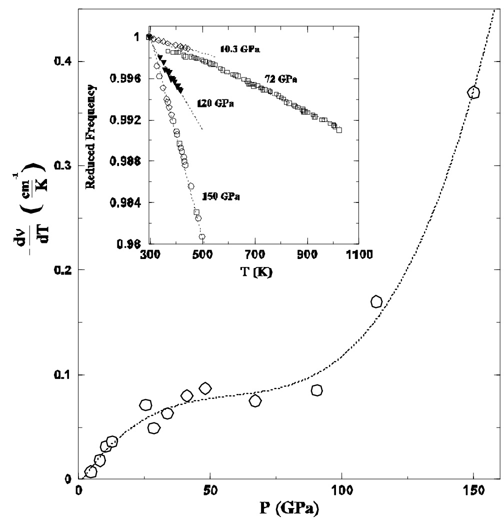

Fig. 2. A temperature derivative of the vibron frequency versus pressure. The solid line is a guide to the eye. Insert: reduced vibron frequencies as a function of temperatures for different pressures.

References:

1. J. Kohanoff, *J. Low Temp. Phys.*, **122**, 297 (2001), and references therein.
2. A. F. Goncharov, E. Gregoryanz, R. J. Hemley, and H.-K. Mao. *PNAS* **98**: 14234 (2001).
3. P. Loubeyre, F. Occelli and R. LeToullec, *Nature* (London), **416**, 613 (2002).
4. E. Gregoryanz, A. F. Goncharov, K. Matsuishi, H.-K. Mao and R. J. Hemley, *PRL*, submitted.
5. F. Datchi, P. Loubeyre, and R. LeToullec, *Phys. Rev. B* **61**, 6535 (2000).
6. V. Diatschenko *et al.*, *Phys. Rev. B* **32**, 381 (1985).
7. O. Pfaffenzeller and D. Hohl, *J. Phys.: Condens. Matter* **9**, 11023 (1997).
8. S. Scandolo, *Proc. Nat. Acad. Sci.*, in press.